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Letter

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High-Energy and High-Power-Density Potassium Ion Batteries Using Dihydrophenazine-Based Polymer as Active Cathode Material

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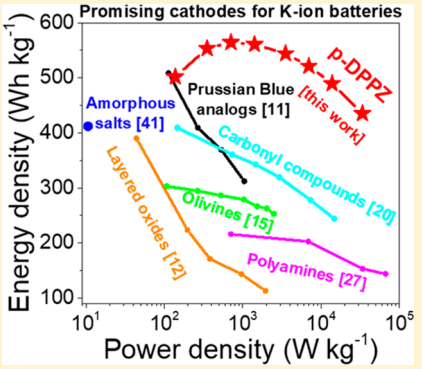
Supporting Information

ABSTRACT: Polymeric aromatic amines were shown to be very promising cathodes for lithium-ion batteries. Surprisingly, these materials are scarcely used for designing post-lithium batteries. In this Letter, we investigate the application of the high-voltage poly(*N*-phenyl-5,10-dihydrophenazine) (p-DPPZ) cathodes for K-ion batteries. The designed batteries demonstrate an impressive specific capacity of 162 mAh g^{-1} at the current density of 200 mA g^{-1}, operate efficiently at high current densities of 2−10 A g^{-1}, enabling charge and discharge within ∼1−4 min, and deliver the specific capacity of 125−145 mAh g^{-1} with a retention of 96 and 79% after 100 and 1000 charge−discharge cycles, respectively. Finally, these K-ion batteries with polymeric p-DPPZ cathodes showed rather outstanding specific power of >3 × 10^4 W kg^{-1}, thus paving a way to the design of ultrafast and durable high-capacity metal-ion batteries matching the increasing demand for high power and high energy density electrochemical energy storage devices.



For decades, lithium-ion batteries have remained the leading technology in the market of electrochemical energy storage devices.[1] However, a low abundance of lithium in the Earth's crust[2] hinders the potential application of this technology with respect to massive scale-up adoption, for example, for bulk energy storage. A significant concern is that the rapid growth and production of various portable electronics and electric vehicles utilizing lithium-ion battery materials as a power source will cascade to the depletion of lithium reserves[3] and a significant increase in prices for lithium and other elements such as Co and Ni.[4]

These circumstances have boosted interest in and provided an impetus for the development of efficient post-lithium electrochemical energy storage technologies that do not involve supply limited elements such as lithium, cobalt, nickel, and other transition-metals. Potassium-ion batteries represent one of the most promising research directions, as indicated by the exponential growth in the number of relevant publications.[5] Indeed, there are virtually unlimited resources of potassium in the Earth's crust and oceans compared with lithium, which dictates a much lower price of this element.[6] Additionally, potassium has a lower redox potential[6] and demonstrates higher diffusion coefficient than sodium due to solvation effects in electrolytes. Another important advantage of potassium over sodium is its ability to intercalate into graphite, which is undoubtedly the cheapest and most widely used anode material for rechargeable metal-ion batteries.[7]

We note that in the development of K-ion batteries, Prussian blue (PB) analogs[8−11] represent the most intensively studied family of cathode materials for K-ion batteries due to their availability, impressive practical energy densities (up to 509 Wh kg^{-1}), high redox potentials, satisfactory rate capabilities, and cycling stabilities. The highest capacity of 148 mAh g^{-1} was reported by Piernas-Muñoz et al.[9] for $K_{1.59}Fe_{2.20}(CN)_6$, although it utilized sodium-based electrolyte $NaPF_6$. Among the truly potassium-ion batteries, the highest practical gravimetric capacity of 142 mAh g^{-1} was demonstrated for $K_{1.89}Mn[Fe(CN)_6]_{0.92}{\cdot}0.75H_2O$.[11]

Besides the PB analogs, various layered transition-metal oxides are also explored as high-capacity cathode materials for potassium-ion batteries.[12−14] For example, the capacities of 178[12] and 140[13] mAh g^{-1} were achieved for $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$ and P3-type $K_{0.5}MnO_2$, respectively. However, this group of materials suffers from poor rate capability and cycling stability

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and low average discharge potentials of <3 V. Olivines[15,16] represent another promising family of cathode materials for potassium-ion batteries, demonstrating excellent cycling stabilities, good rate capabilities, and high discharge potentials of >3.9 V. Unfortunately, these materials show inferior gravimetric capacities and energy densities in comparison with the PB analogs and layered transition-metal oxides. Indeed, the specific capacity of 73 mAh/g reached for $KVOPO_4$ represents one of the highest values reported for this group of materials.[15]

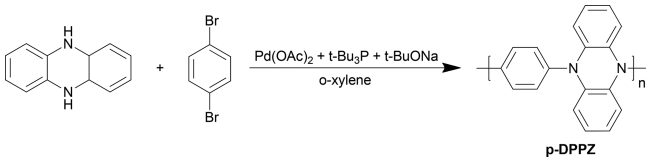
Organic redox-active compounds are actively explored as a highly promising alternative to conventional inorganic cathodes for metal-ion batteries. Indeed, organic materials are composed of abundant elements such as C, H, N, O and S, forming the fundamental basis of all living organisms on our planet. Organic materials can be produced entirely from renewable resources. In addition, batteries based on organic materials and containing no heavy metals in their structure can be utilized and recycled as an ordinary household waste. Therefore, organic batteries can be considered as an environment-friendly solution for electrochemical energy storage.

Importantly, light chemical elements forming organic redox-active species can enable potentially much higher specific capacities compared with standard cathodes based on inorganic oxides and other inorganic polyanion compounds. Organic compounds have already shown an impressive performance in lithium-ion and sodium-ion batteries,[3,17−19] yet organic cathodes for potassium-ion batteries are still in the infancy of their development.[5−7] Among the very few reported examples, carbonyl compounds have demonstrated the best characteristics to date.[20−24] Recently, a specific capacity of 260 mAh g^{-1} was delivered by poly(pentacenetetraonesulfide) (PPTS) cathodes operating at a low current density (100 mA g^{-1}), whereas a very decent value of 167 mAh g^{-1} was reached at a high current density of 10 A g^{-1}.[20] The main drawback of carbonyl compounds is their low discharge potential of ∼2 V, which severely limits the achievable energy density, which is the main figure of merit for energy storage devices.

The problem of low discharge potentials can be solved using other families of organic redox-active compounds such as nitroxyl-based radical-ion polymers, conductive polymers (e.g., polyaniline or polypyrrole), and polymerized aromatic amines.[25,26] Amine-based polymers offer exceptional promise as organic cathodes for metal-ion batteries because they can potentially deliver high specific capacities in addition to optimal discharge potentials of ∼4 V, excellent rate capability, and good operation stability.[26−28] However, among all known polymeric arylamines, only poly(*N*,*N*′-diphenyl-*p*-phenylenediamine) (PDPPD)[28] and polytriphenylamine (PTPA)[29] were previously explored as cathodes for K-ion batteries, with decent reported specific capacities and energy densities of up to 63 mAh g^{-1} and 216 Wh kg^{-1}. However, a much broader range of rationally designed materials should be investigated to unravel a full potential of polyarylamine-type cathodes in potassium batteries.

Herein we investigated poly(*N*-phenyl-5,10-dihydrophenazine) (p-DPPZ[30]) and demonstrated that it represents one of the most promising organic cathode candidates for K-ion batteries. We synthesized p-DPPZ following the originally reported method[30] based on the reduction of phenazine to 5,10-dihydrophenazine and the following Buchwald−Hartwig condensation of the latter with 1,4-dibromobenzene (Scheme 1, details are given in the Supporting Information).

Scheme 1. Synthesis of p-DPPZ



The electrochemical tests were performed using two-electrode CR2032 coin-type cells with the working electrode based on the p-DPPZ composite with super-P conductive carbon filler and polyvinylidene difluoride (PVDF) binder deposited on the Al current collector while the metallic potassium was serving as the anode. (The details are provided in the Supporting Information).

Carbonate-based electrolytes represent the gold standard for lithium-ion batteries. In particular, the commercially available 1 M $LiPF_6$ in a 1:1 v/v mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) is the electrolyte formulation most commonly used in research laboratories due to its high ionic conductivity and good electrochemical stability (window up to 4.3 V),[31] which enable efficient battery operation with the vast majority of known cathode materials. On the contrary, we note that there is no universal electrolyte formulation suitable for various potassium-ion batteries. Frequently, cathode materials for K-ion batteries possess high redox potentials and additionally show considerable overpotentials (Coulombic inefficiencies) toward charge and discharge cycles. Therefore, higher overvoltages have to be applied beyond the stability window of carbonate-based electrolytes to achieve the full charge and discharge states in such batteries. There is also an opinion that solid electrolyte interfaces (SEIs), in particular, formed at the anode, are not stable in the case of using carbonate-type electrolytes.[32] However, the impacts of solvent and electrolyte salts on the properties of SEIs formed in K-ion batteries during their operation remain poorly understood. Yet, from previous work in our group and others on K-ion batteries, we have found that diglyme (DG), 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), and fluorinated carbonates (e.g., fluoroethylene carbonate (FEC)) are generally suitable as the most preferred electrolyte solvents.[32−36]

In this work, we show that the choice of an appropriate electrolyte represents a crucial issue for achieving a superior performance of K-ion batteries with p-DPPZ cathodes. To find an optimal solution, a broad range of the electrolyte formulations were screened, as shown in Figure 1. In short, KPF_6 solutions in a 1:1 v/v mixture of EC with diethylcarbonate (EC/DEC), 1:1 v/v mixture of FEC/DMC, as well as in pure DG and DME were chosen as basic electrolyte formulations for K-ion batteries with p-DPPZ cathodes. We note that low cycling stability and poor rate capabilities were observed for the cells assembled with 0.5 M KPF_6 in EC/DEC, which is in line with the previously reported results for this electrolyte composition.[31] On the contrary, 1 M KPF_6 solution in FEC/DMC afforded the highest specific capacity at the lowest current density of 40 mA g^{-1}, but it strongly decayed at higher current densities. The 1 M solution of KPF_6 in DG showed a superior performance compared with 1 M KPF_6 in DME. It is known that using highly concentrated electrolyte solutions usually improves the overall performance of potassium batteries.[37−39] DG was chosen as the solvent for KPF_6 salt, which allowed for the preparation of a 2.2 M concentration of the electrolyte.

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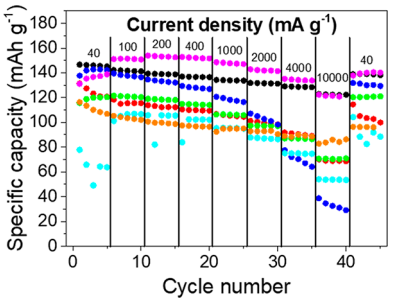

Figure 1. Capacity versus current density behavior of p-DPPZ//K half-cells with different electrolyte formulations: 0.5 M KPF_6 in EC/DEC (red), 1 M KPF_6 in diglyme (green), 1 M KPF_6 in FEC/DMC (blue), 1 M KPF_6 in DME (cyan), 2.2 M KPF_6 in diglyme (magenta), and 2 M KTFSI in diglyme (orange). Characteristics of the p-DPPZ//Li half cells with 1 M $LiPF_6$ in EC/DMC electrolyte are shown for comparison (black).

The cells assembled with a 2.2 M solution of KPF_6 in DG demonstrated strongly improved performance. The specific capacity of the cells was rapidly growing during the initial few cycles, suggesting the reorganization of the system, which is tentatively associated with a high viscosity of the electrolyte, limiting the rate of its penetration into the cathode composite. The capacity increased at higher current densities, reaching the maximal value of 154 mAh g^{-1} at 200 mA g^{-1}. Replacing the KPF_6 with potassium bis(trifluoromethylsulfonyl)imide (KTFSI) while preserving the ~2 M salt concentration did not improve the results, suggesting that the smaller hexafluorophosphate anion probably has better compatibility with the p-DPPZ cathode framework because anions are penetrating into the polymer cathode while charging.

Particular attention should be paid to the high rate capability revealed by the cells with the 2.2 M KPF_6 in DG electrolyte, demonstrating exceptional specific capacities of 122−135 mAh g^{-1} at current densities as high as 4−10 A g^{-1}. Interestingly, the K-ion cells in terms of specific capacity and energy density even surpassed the reference Li-ion cells assembled using 1 M $LiPF_6$ in EC/DMC (1:1 v/v). The obtained results clearly indicate that 2.2 M KPF_6 in DG represents the optimal electrolyte composition for K-ion batteries comprising p-DPPZ cathodes.

Cyclic voltammetry (CV) measurements (Figure 2) demonstrate that the potential range of 2.5−4.5 V should be considered as optimal for charge−discharge cycling of batteries with p-DPPZ cathodes. The first cycle revealed the group of irreversible oxidation peaks in the range of 3.8 to 4.5 V, which can be attributed to SEI formation processes. X-ray photoelectron spectroscopy (XPS) confirmed that SEI was indeed formed atop the p-DPPZ cathode after the first charge/discharge cycle. This SEI incorporated multiple C−O bonds from the electrolyte solvent in combination with KF, most probably released from KPF_6 (Figure S2).

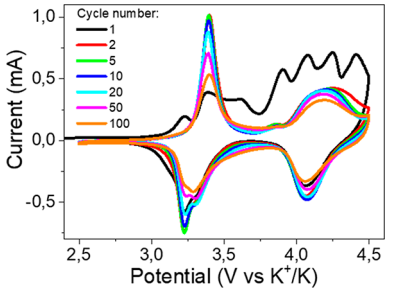

Figure 2. Cyclic voltammograms of p-DPPZ//K half-cell with 2.2 M KPF_6 in diglyme electrolyte.

Starting from the second cycle, the CV profile exhibits a pair of well-defined narrow redox peaks with a half-wave potential $E_{1/2}$ of 3.31 V due to a single electron oxidation of each of the dihydrophenazine units. This process can also be interpreted as the conversion of every second 1,4-phenylenediamine moiety in the main polymer chain to the corresponding quinoneimine (Scheme 2). Another set of broad peaks with $E_{1/2}$ = 4.16 V is rather typical for (quasi)conjugated polymers[28] and corresponds to the further oxidation of each of the monomer units in p-DPPZ, thus converting all *1,4*-phenylenediamine fragments to quinoneimines (Scheme 2). The presence of some additional minor redox peaks with an evident splitting of the main reduction peak at 3.23 V is apparently related to the unavoidable polydispersity and the presence of defect sites or end-capping groups in the polymer chains, which show a somewhat different electrochemical behavior due to the different chemical "surroundings".

The electrochemical behavior of p-DPPZ cathode was further investigated by the galvanostatic charge−discharge cycling of K//p-DPPZ half-cells assembled using the optimized electrolyte (2.2 M KPF_6 in DG) in the voltage range of 2.5−4.5 V (Figure 3). Two discharge plateaus at 4.1 and 3.3 V can be distinguished on the charge−discharge curves (Figure 3a), which is in a good agreement with the CV data. The average cell discharge potential of ~3.6 V was considerably higher than that of all previously reported K-ion batteries with organic cathodes. Moreover, this value is comparable to the discharge potentials of the most promising inorganic cathodes based on PB analogs.

The p-DPPZ cathodes also demonstrated high gravimetric capacities of 155, 142, and 127 mAh g^{-1} in the first cycle while charged and discharged at current densities of 200, 400, and 1000 mA g^{-1}, respectively (Figure 3b). The highest capacity of 162 mAh g^{-1} was achieved at the current density of 200 mA g^{-1} (~1 C rate), which exceeds the best values delivered by the commonly used lithium-ion batteries with $LiFePO_4$ cathodes operating even at lower discharge rates.[40] This example illustrates that cheaper potassium-ion batteries with organic cathodes are now demonstrating a comparable performance to the industrial Li-ion benchmarks.

Notably, p-DPPZ cathodes show some initial activation reflected in a gradual improvement of the specific capacity and Coulombic efficiency within the first 10−20 cycles. We believe that such behavior is associated with the use of a concentrated and viscous electrolyte, which likely slowly penetrates into the cathode framework upon cycling. Indeed, using less concentrated 1 M KPF_6 in DG as the electrolyte significantly suppressed this activation behavior (Figure 1). Alternatively, reduced specific capacity and Coulombic efficiency can be associated with the formation of SEI atop p-DPPZ cathodes, as revealed by XPS (Figure S2). Moreover, the behavior of the Coulombic efficiency in the initial cycles is strongly electrolyte-dependent, which also points to the irreversible processes leading to the SEI formation (Figure S3).

In terms of cyclability, the p-DPPZ//K cells showed a decent capacity retention of 92 (200 mA g^{-1}), 93 (400 mA g^{-1}), 95 (1000 mA g^{-1}), and 96% (2000 mA g^{-1}) after 100 charge/discharge cycles (Figure 3c). While cycling the

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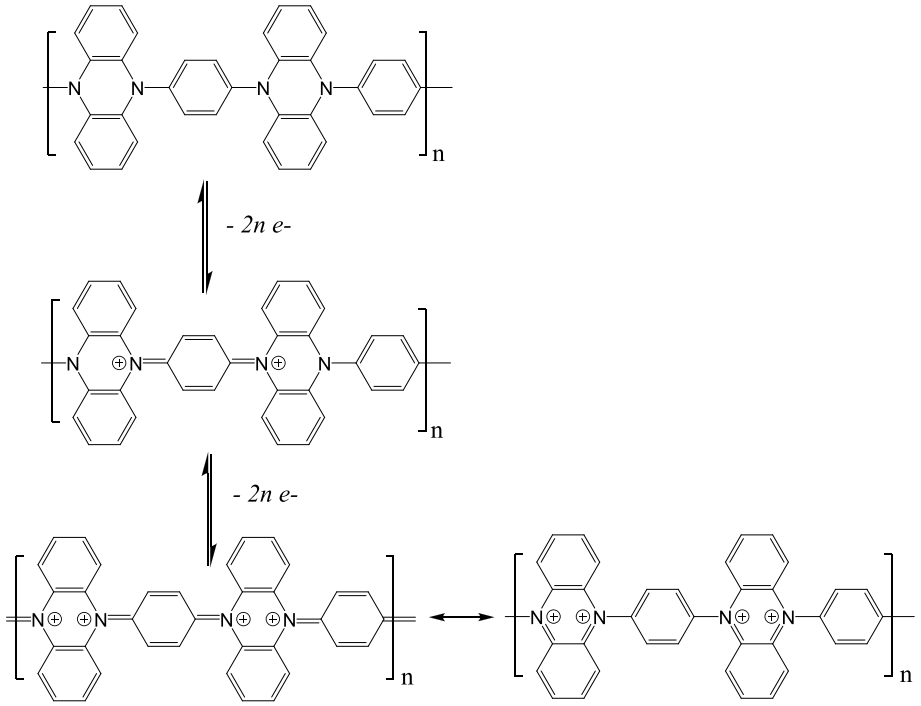
Scheme 2. Redox Transformations of p-DPPZ



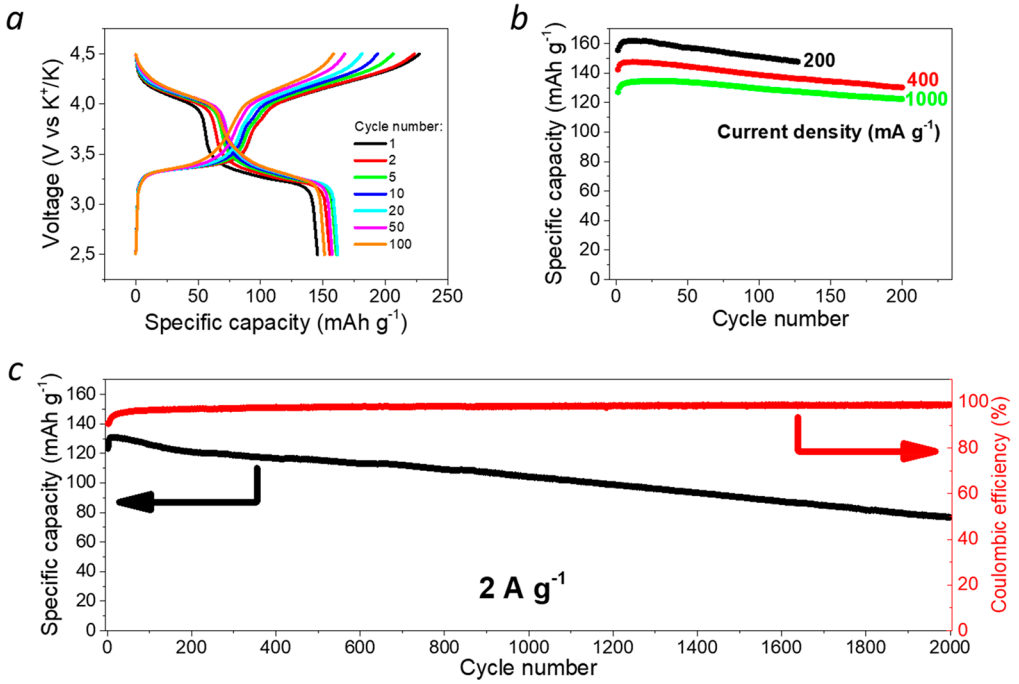


Figure 3. Electrochemical characteristics of K-ion batteries with p-DPPZ cathode and 2.2 M KPF_6 in diglyme electrolyte cycled in the voltage range of 2.5−4.5 V: (a) charge−discharge characteristics at 200 mA g^{-1} current density, (b) evolution of specific capacity under cycling at different current densities, and (c) long-term cycling stability of cell at current density of 2 A g^{-1}.

batteries at high current density of 2 A g^{-1}, the maximum specific capacity was 131 mAh g^{-1} with a retention of 79 and 59% of this value after 1000 and 2000 cycles, respectively. The Coulombic efficiency was maintained at 99 to 100% for at least 2000 cycles at 2 A g^{-1}. The observed gradual capacity decay is most likely related to the partial dissolution of the cathode material in the electrolyte, as was concluded from the appearance of a colored substance on the separator of the battery disassembled after ∼1000 cycles (Figure S1). We strongly believe that the operational stability of these batteries can be substantially improved upon further optimization of the synthesis of the material and battery manufacturing technology.

p-DPPZ//K cells with the optimized electrolyte demonstrated a rather remarkable rate capability. Figure 4a shows charge−discharge curves recorded at different current densities. The specific capacity decreases from ∼153 to 123 mAh g^{-1} while the current density is increased 50-fold from

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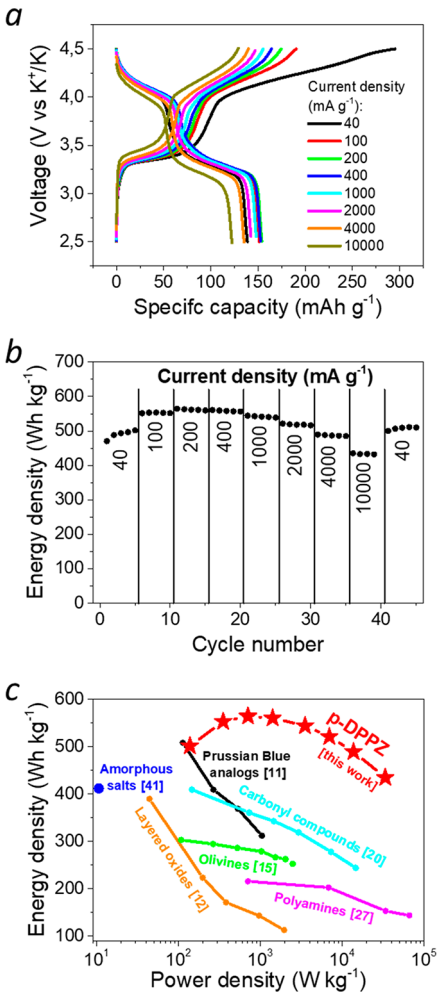

Figure 4. (a) Charge−discharge characteristics and (b) energy density of K-ion batteries with p-DPPZ cathode at different current densities. (c) Chart showing the energy density versus power density performance of p-DPPZ polymeric cathode reported here compared with the best literature benchmarks of organic and inorganic cathodes reported so far for K-ion batteries.

200 mA g^{-1} to 10 A g^{-1}. Because the current density of 10 A g^{-1} corresponds to ~80 C rate (considering the practical specific capacity), the full charge or discharge of the battery can be performed in <1 min. There is a strong demand for such ultrafast batteries to match the current level of the development of various portable electronics and electric vehicles, which need the batteries to be charged in minutes rather than hours.

Figure 4b shows that p-DPPZ//K batteries deliver the highest energy density of 564 Wh kg^{-1} at the current density of 200 mA g^{-1} (~1 C current rate). Champion cells showing the specific capacity of 162 mAh g^{-1} (Figure 3b) provide an even higher energy density of 593 Wh kg^{-1}. To the best of our knowledge, these are record values among all reported inorganic and organic cathodes evaluated so far in K-ion batteries. Furthermore, the revealed performance of p-DPPZ//K cells in the context of both energy and power density is particularly exciting, as one can conclude from the comparison chart shown in Figure 4c. The demonstrated power density of >10^4 W kg^{-1} makes the p-DPPZ//K batteries behaving similarly to supercapacitors while still maintaining the high-energy density of metal-ion batteries.

In summary, we have demonstrated for the first time that polyarylamine p-DPPZ as a cathode for K-ion batteries with an optimized electrolyte composition can achieve record-high performance characteristics for this new type of energy storage devices. Indeed, p-DPPZ delivered superior energy and power density in combination with a good operation stability during charge/discharge cycling, which are the most important prerequisites for considering further practical applications. Importantly, p-DPPZ in potassium-ion cells showed a comparable energy density to that of conventional $LiFePO_4$ cathodes, which are massively used in the lithium battery industry. This clearly illustrates that the rapid development of K-ion batteries has now brought them very close to the Li-ion industrial benchmarks. In that context, the design of advanced organic cathodes such as p-DPPZ reported here might play an important role in the commercialization of the emerging K-ion battery technology.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b02039.

Experimental procedures and methods for material synthesis, cathode fabrication, cell assembling, and electrochemical testing (PDF)

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Notes

The authors declare no competing financial interest.

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